

AD-A097 223

AKRON UNIV OH INST OF POLYMER SCIENCE

F/6 11/9

THE ROLE OF CHEMICAL BONDING IN THE ADHESION OF ELASTOMERS.(U)

APR 81 A N GENT

N00014-76-C-0408

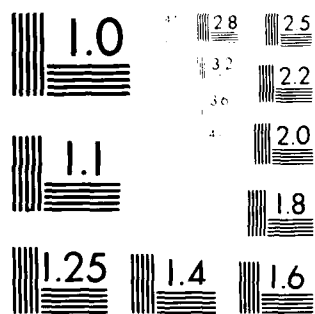
UNCLASSIFIED

TR-11

NL

1 1 1
AD A
59 500 3

END
DATE
FILMED
5-81
DTIC



MICROCOPY RESOLUTION TEST CHART
 NATIONAL BUREAU OF STANDARDS-1963-A

LEVEL II

(12)

AD A 097223

OFFICE OF NAVAL RESEARCH

Contract N00014-76-C-0408 ✓

Project NR 092-555

Technical Report No. 11 ✓

THE ROLE OF CHEMICAL BONDING IN THE ADHESION OF ELASTOMERS

by

A. N. Gent

Institute of Polymer Science
The University of Akron
Akron, Ohio 44325

DTIC
ELECTE
S APR 02 1981 D
F

April, 1981

Reproduction in whole or in part is permitted
for any purpose of the United States Government

Approved for Public Release; Distribution Unlimited

DTIC FILE COPY

81 4 2 148

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report 11	2. GOVT ACCESSION NO. AD-A097223	3. RECIPIENT'S CATALOG NUMBER 14 TR-11
4. TITLE (and Subtitle) The Role of Chemical Bonding in the Adhesion of Elastomers.		5. TYPE OF REPORT & PERIOD COVERED Technical Report
6. AUTHOR(s) A. N./Gent		7. PERFORMING ORG. REPORT NUMBER N00014-76-C-0408
8. PERFORMING ORGANIZATION NAME AND ADDRESS Institute of Polymer Science The University of Akron Akron, Ohio 44325		9. CONTRACT OR GRANT NUMBER(s) NR 092-555
10. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Power Program Arlington, Virginia 22217		11. REPORT DATE Apr 1978
12. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 26
		14. SECURITY CLASS. (of this report) Unclassified
15. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES Submitted for publication in: International Journal of Adhesion and Adhesives		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Adhesion, Bonding, Crosslinking, Elastomers, Fracture, Interface, Oxidation, Silanes, Strength, Surfaces.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A review is given of several studies of the effect of interfacial bonding upon the mechanical strength of an adhesive joint. In the first, polybutadiene layers were crosslinked by a free radical process whilst in contact with silane-treated glass. A direct proportionality was found between the minimum peel strength of the joint, as high temperatures and low rates of peeling, and the vinyl content of the silane treatment liquid. Covalent bonding between the diene polymer and vinyl groups on the treated glass was inferred. When radioactively tagged silanes were employed, extensive combination with the		

DD FORM 1 JAN 75 1473

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

451661

glass substrates was demonstrated. Again, the greater the amount of vinyl silane found on the treated glass surface, the greater the mechanical strength of adhesion between the treated glass and a polybutadiene overlayer. In another series of experiments two partially-crosslinked sheets of polybutadiene were pressed together before the crosslinking was taken to completion. The additional crosslinking was determined from measurements of the elastic properties and of the degree of equilibrium swelling by a compatible liquid. Again, the mechanical strength of adhesion between the two sheets under threshold conditions was found to be directly proportional to the inferred degree of interfacial interlinking. Thus, at least at high temperatures and low rates of peel, there is substantial evidence for a direct correlation between the mechanical strength of a joint and the degree of interfacial chemical bonding. Moreover, the relationships established in these studies allow other bonding systems to be diagnosed as chemical or physical in nature. For example, a dramatic increase in the strength of adhesion between two cross-linked polybutadiene layers was observed if they were exposed to air or oxygen for periods of an hour or two before being pressed into contact. It is inferred that interfacial chemical bonds are formed as a consequence of rapid surface oxidation reactions.

The Role of Chemical Bonding in the Adhesion of Elastomers

A. N. Gent

Introduction

Although coupling agents are widely employed in an attempt to form chemical bonds between adherends, the real nature of the interface and the extent of chemical coupling achieved is generally rather uncertain. Indeed, it has been questioned whether interfacial chemical bonds are formed at all (1). It has been suggested that a strong joint would be developed from dispersion forces alone (2) and that covalent bonding at the interface is not really necessary. It has also been suggested that a high density of interfacial bonding would be detrimental, making the joint brittle and weak (3). On the other hand, for adhesive joints between polymers and metal or glass that are able to withstand severe conditions of high temperature and high humidity, it has been found advantageous to employ coupling agents or adhesion promoters with dual functionality, capable of interlinking the two adherends (4).

Thus, the chemist is presented with a fundamental dilemma in designing composites:

Is it a good idea to form chemical bonds across the interface, or is it not?

And if chemical bonding is advantageous, is there a certain degree of chemical bonding that will confer maximum strength on the composite?

In view of these fundamental questions, it seemed

on For	
Final	<input checked="" type="checkbox"/>
Used	<input type="checkbox"/>
ation	<input type="checkbox"/>
ation/	
ility Codes	
Avail and/or	
Special	
Dist	<input checked="" type="checkbox"/>

worthwhile to carry out a detailed study of the strength of some model adhesive joints in which the degree of interfacial bonding could be varied over a wide range (5 - 8). These studies, carried out over a period of several years, are the subject of the present review. As a result of them, it has become clear that chemical bonding at the interface is, indeed, a strengthening feature, but that it must take a particular form, using long extensible molecules as interfacial ties, to be most effective. Finally, some recent work is described on interfacial chemical bonds that are formed as a consequence of surface oxidation reactions in polybutadiene (9). This work provides a striking example that even small amounts of interfacial bonding can cause dramatic increases in adhesion.

Test Methods for Studying the Adhesion of Elastomers

In order to study the influence of interfacial bonding on the mechanical strength of an adhesive joint, it is necessary to minimize all other contributions to the observed strength. The measured strength of adhesive joints is larger for ductile, inelastic, and viscoelastic adhesive materials than it is for purely elastic materials, because any work expended irreversibly in stressing the joint up to the point of failure is included in the total work of detachment. In order to focus attention on inter-

facial bonding, therefore, we must employ purely elastic adherends. We have chosen a model material which comes close to this ideal. It is a simple high-molecular-weight elastomer, polybutadiene, which can be applied to substrates as a thin liquid layer and then lightly crosslinked in situ, to form a soft elastic layer.

After polybutadiene is crosslinked it can no longer undergo liquid-like flow. However, it is still not perfectly elastic because there is a measurable degree of internal friction between molecular segments. This internal friction can be minimized by raising the test temperature, so that molecular Brownian motion is more rapid, and by detaching the adhering layer at very low speeds. Under these conditions, namely at low rates of peeling and at high test temperatures, the adhering polybutadiene layer is almost perfectly elastic.

Moreover, because it is a soft material the tendency to set up interfacial stresses as a result of differential thermal expansion and contraction is quite small. Indeed, in one series of experiments no interfacial stresses at all were set up as a result of thermal expansion or of swelling because the testpiece employed was perfectly symmetrical (8). It consisted of two identical polybutadiene layers, bonded together, as shown schematically in Figure 1 and discussed in detail later.

In all cases the strength of adhesion was determined

by a peeling experiment, Figures 1 and 2. The work W_a of separation per unit area of interface was calculated from the peel force per unit width of the test specimen,

$$W_a = 2F/w.$$

Bonding Polybutadiene to Glass with Silane Coupling Agents (5 - 7)

The surface density of interfacial chemical bonds between a glass substrate and a lightly-crosslinked layer of polybutadiene elastomer can be varied by first treating the glass with a mixture of vinyl and ethyl silanes (5). It is assumed that vinyl groups added to the glass are capable of bonding to a polybutadiene layer during a free-radical crosslinking reaction of the latter (Figure 3) , whereas the ethyl silane groups are assumed to be quite unreactive towards polybutadiene. In agreement with this assumption, it was found that the resistance to peeling the polybutadiene layer from the glass substrate increased in direct proportion to the amount of vinyl silane used for treating the glass, Figure 4 (5).

Under near-equilibrium conditions; that is, at low rates of peeling and at high temperatures, the threshold levels of adhesion increased from about 1 J/m^2 for no interfacial covalent bonding, with only ethyl silane groups on the glass surface, to about 40 J/m^2 with all vinyl silane groups on the glass, Figure 4. This large

increase in peel strength is attributed to interfacial bonding. Direct evidence for the presence of silane groups on the glass surface has been obtained by radiochemical techniques (7), and, again, the greater the concentration of vinyl silane groups, the stronger was the elastomer-glass adhesive bond.

The factor of improvement between all ethyl and all vinyl silane treatments, about 40 times, is comparable in size to the relative strengths of covalent bonds in comparison with dispersion bonds. However, the absolute magnitudes of the peel strength, both for no covalent bonding, 1 J/m^2 with ethyl silane, and with some unknown degree of interfacial bonding, about 40 J/m^2 with vinyl silane, are much greater than can be accounted for on theoretical grounds, using the surface energies associated with non-polar dispersion forces and the dissociation energies for covalent bonds. The discrepancy is about a factor of 20 in both cases, the measured threshold strength being about 20 times larger than theory would predict both for dispersion and covalent bonding. We attribute this discrepancy to the polymeric character of the elastomeric adherend: many molecular bonds in a polymer molecule attached to the substrate must be stressed before it will become detached (10). Thus, a polymeric adhesive with long extensible molecules connecting to a substrate will be much stronger than a rigid or highly-

crosslinked material. In agreement with this hypothesis, the strength of adhesion to glass was found to decrease with increasing crosslinking of the polybutadiene overlayer, as the molecular sequences between points of interlinking were reduced in length and the number of molecular bonds subjected to an equal stress was decreased (5).

Bonding Polybutadiene to Itself by Free-Radical Crosslinking (8)

The major advantage of the next experimental arrangement is that the density of interlinking between the two components can be inferred with some confidence from the known chemistry of homogeneous crosslinking reactions in elastomers.

The test procedure is as follows: two identical layers of an elastomer are prepared, partially crosslinked ("cured") to the same extent. These layers are then pressed into intimate contact and the crosslinking reaction is taken to completion, Figure 1. By varying the extent of crosslinking before the layers are brought into contact, the degree of chemical interlinking can be varied over the entire range, from zero, when two fully-cured sheets were pressed together, up to a level characteristic of the density of crosslinking within a fully-cured sheet when the layers are brought together before any crosslinking takes place. Moreover, the

density of crosslinking within simple elastomer systems can be determined at various stages in the crosslinking process. We have employed measurements of elastic behavior and equilibrium swelling in n-heptane to provide estimates of the degree of crosslinking at various times of reaction and hence of the degree of interlinking when two sheets are brought together after partial crosslinking and then the crosslinking reaction is taken to completion.

Again, the test material used in these experiments was polybutadiene, and for the same reasons as before. It is relatively pure, non-polar and non-crystallizing. It crosslinks readily by a free-radical mechanism, with small amounts of dicumyl peroxide. It has an extremely low glass transition temperature of about -95°C and hence experiments can be carried out under near-equilibrium conditions at moderate temperatures.

Because the two-layer testpiece is symmetrical, no shrinkage stresses are developed on warming or cooling. Furthermore, the testpiece could be swollen uniformly by compatible liquids so that the dissipative properties of the elastomer were reduced still further, without introducing stresses at the interface. Thus, measurements of the mechanical strength could be made using swollen testpieces to test the hypothesis that a constant low value is attained in the absence of mechanical energy

dissipation within the adherends, and that it is this threshold value which is directly related to the degree of interfacial bonding.

Measurements of the strength of adhesion are shown in Figure 5 where the work \underline{W}_a of detachment is plotted against the rate \underline{R} of peeling. These measurements were carried out at a temperature of 100°C to minimize visco-elastic contributions to the observed peel strength. At the lowest rates of peeling the results do, indeed, approach asymptotically towards threshold values, which range from 5 to 60 J/m², depending upon the degree of chemical interlinking. Moreover, the same minimum values were obtained with swollen test pieces, denoted by open circles in Figure 5, when allowance was made for the reduced density of molecular strands in the swollen material by the areal factor λ_s^2 , where λ_s is the linear swelling ratio. In these experiments the time \underline{t}_1 of crosslinking the two sheets separately before they were brought together for subsequent reaction for a further time \underline{t}_2 was varied from 0 to 90 minutes. The sheets were fully crosslinked after 90 minutes and, therefore, the lowest curves in Figure 5 represent adhesion with little or no chemical interlinking. On the other hand, the uppermost curves represent zero time of crosslinking of the sheets separately, and full crosslinking together. In this case, the interlinking takes place to the same

extent as the crosslinking within each sheet so that they become fused into one homogeneous sheet and the peeling experiment consists of tearing through a single block.

In Figure 6, values of the detachment energy \underline{W}_a determined under threshold conditions, obtained by extrapolating experimental values over a wide range of peel velocities to a zero-velocity condition, are plotted against the increase Δv in the density of network strands due to further crosslinking whilst the sheets were in contact. Δv is employed as a measure of the amount of interlinking. It was determined by means of the Flory-Huggins theoretical relation between equilibrium swelling and density v of network strands in a crosslinked elastomer (11). As can be seen, the threshold strength of adhesion was found to increase in direct proportion to the degree of interfacial bonding, from very low values up to the measured cohesive tear strength, denoted by open circles for the two levels of crosslinking employed in these experiments. Thus, there appears to be a direct proportionality between the mechanical strength obtained under threshold conditions and the density of chemical bonding between the two elastomer layers.

It is noteworthy that the sheets prepared with 0.2 percent dicumyl peroxide crosslinking agent were weaker under all circumstances than the sheets prepared with a smaller amount of dicumyl peroxide. They were weaker in

adhesion and weaker in cohesion, in the fully-reacted state. This observation again points to the importance of the length of the molecular sequences composing an adhesive. When the molecular ties are long, they contain a large number of bonds, all of which must be stressed highly in order to break one of them. When the material is highly crosslinked and the molecular sequences are short, then it is both less extensible and weaker.

Bonding Polybutadiene to Itself by Surface Oxidation Reactions (9)

An unusual bonding process has recently been encountered. Extremely strong bonding has been observed between some fully-crosslinked polybutadiene sheets when they were exposed to air for short periods at room temperature before being pressed together. In some cases the two sheets could not later be separated. The experiments were carried out as follows.

Thin sheets were prepared between layers of a polyester film (Mylar film, from E. I. duPont de Nemours and Co.). The Mylar film was then removed from each of the two sheets, exposing the elastomer surfaces to air. After a given period of time two elastomer surfaces were brought into contact and pressed together under a light force for a further period, generally 24 hours, at room temperature. This procedure is shown schematically in Figure 7. The strength of adhesion was then measured by

peeling the adhering strips apart.

All of these peel tests were carried out at room temperature and at a peel rate of 80 $\mu\text{m/s}$. These conditions are not sufficiently gentle to eliminate viscoelastic contributions to the work of detachment altogether. Only a qualitative interpretation of the experimental results is, therefore, attempted.

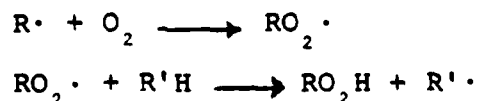
As shown in Figure 8, the strength of self-adhesion of crosslinked strips of polybutadiene depended strongly upon the period of exposure to air before they were brought into contact. Initially rather low, the peel strength rose dramatically as the period of exposure to air increased, so that after exposure for 1-2 hours before the strips were pressed together, they could not be separated without tearing the elastomer layers. For exposure periods greater than about 2 hours the subsequent adhesion became weaker, and it fell rapidly as the exposure time was increased still further. Eventually, after exposure periods of about 10 days, the self-adhesion of the elastomer layers was quite small, comparable to the initial value.

If the protective Mylar films were removed from the elastomer layers in an atmosphere of nitrogen (in a glove box) and the two layers were then pressed together, the resulting strength of adhesion was found to be low and

constant, independent of the period which elapsed between removing the Mylar films and joining the elastomer layers together, Figure 8. Thus, the striking increases, and later decreases, in adhesion shown in the Figure appear to be a result of reaction of polybutadiene with atmospheric oxygen.

In striking contrast to the strong adhesion developed in polybutadiene materials, no comparable effect was observed with natural or synthetic cis-polyisoprene. Indeed, the self-adhesion of crosslinked layers of natural rubber was found to be decreased somewhat by prior exposure to air. Now, it is well-known that oxidative reactions lead to further crosslinking and hardening of polybutadiene vulcanizates whereas, in contrast, they generally lead to softening of polyisoprene vulcanizates as a result of molecular scission (12). Thus, the observed adhesion phenomenon is wholly consistent with the development of interfacial bonding by means of oxidative processes in those polymers for which molecular interlinking is the principal result of oxidation.

Oxidation of polyolefins is reported to involve two main propagation steps (12):



In the first, a polymer radical reacts with oxygen to form the peroxy radical which, in the second step, abstracts H from a nearby group to form a hydroperoxide and a second radical. Moreover, the hydroperoxide itself decomposes slowly, generating further radical species, so that the process is autocatalytic.

Now, this general reaction scheme does not account for crosslinking and hardening during oxidation. Another reaction must therefore be invoked: the addition of polymer radicals to other polymer molecules to form intermolecular bonds.



This reaction is known to occur in polybutadiene by addition to the C-C double bond but not to a significant degree in polyisoprene where the radicals appear to be less reactive. Thus, it can account for the interfacial bonding observed with polybutadiene but not with polyisoprene. Moreover, it will become proportionately greater in importance as the concentration of oxygen becomes lower, i.e., as oxidation continues in the interfacial region after the elastomer layers have been brought into contact. We therefore infer that this radical addition is responsible for the observed adhesion.

Conclusions

Chemical interlinking between two layers of a model elastomer, or between a layer of elastomer and a rigid glass substrate, has been shown to cause large increases in the strength of adhesion. Indeed, the increase in peel strength appears to be approximately proportional to the density of interfacial bonds.

There are three other aspects of this correlation that must be mentioned, however. First, it is most clearly seen under threshold conditions when other contributions to the measured strength arising from internal dissipation processes (viscous processes, ductile flow, plastic yielding, internal cavitation, detachment from filler particles, etc.) are all absent. The effect of interfacial bonding is not so obvious when these other processes are present because they can raise the observed strength of adhesion by as much as 3 or 4 orders of magnitude (13-16).

Secondly, the absolute values of the strength of adhesion, even under threshold conditions, are much larger than simple thermodynamic calculations would suggest. This discrepancy, by a factor of about 20 in our experiments, is attributed to the Lake-Thomas mechanism (10): many molecular bonds must be stressed in order to break or detach a single molecular chain

in an elastomeric network. In consequence, the greater the degree of internal crosslinking, the weaker the adhesive joint.

Finally, attention has been drawn to an example of inadvertent interlinking, when materials capable of free-radical crosslinking are brought into contact after surface oxidation has started. It is remarkable that strong bonding is obtained when the oxidation process is at an early stage and reveals again that a small number of long, extensible, interlinking molecules can produce strong adhesive joints.

Acknowledgements

This work was carried out in cooperation with Dr. P. Dreyfuss of these laboratories, Dr. A. Ahagon, now at the Yokohama Tire and Rubber Company, Dr. K. C. Sehgal, now at Union Carbide Corporation, Dr. R.-J. Chang, now at the General Tire and Rubber Company, and Mr. C.-C. Hsu, now at the University of Illinois. It was supported initially by a research grant from the Engineering Division of the National Science Foundation (NSF ENG-75-16982) and later by a research grant from the Office of Naval Research (ONR N00014-76-C-0408). An earlier version was presented at the International Congress on Adhesion and Composites, held in Lyon, France, September 11-14, 1979, under the auspices of the Association Nationale de la Recherche Technique.

References

1. W. D. Bascom, *Macromolecules* 6, 792 (1972).
2. J. J. Bikerman, "The Science of Adhesive Joints," Academic Press, New York, 1961.
3. P. W. Erickson, *J. Adhesion* 2, 131 (1970).
4. E. P. Plueddeman, *J. Adhesion* 2, 184 (1970).
5. A. Ahagon and A. N. Gent, *J. Polymer Sci: Polymer Phys. Ed.* 13, 1285 (1975).
6. A. Ahagon, A. N. Gent and E. C. Hsu, "Adhesion Science and Technology," ed. by L.-H. Lee, "Polymer Science and Technology, Vol. 9A," Plenum Press, New York, 1975, pp. 281-288.
7. Y. Eckstein, P. Dreyfuss, Q. S. Lien and H. H. Dollwet, submitted to *J. Polymer Sci: Polymer Letters Ed.*
8. R.-J. Chang and A. N. Gent, submitted to *J. Polymer Sci: Polymer Phys. Ed.*
9. R.-J. Chang, A. N. Gent, C.-C. Hsu and K. C. Sehgal, *J. Appl. Polymer Sci.* 25, 163 (1980).
10. G. J. Lake and A. G. Thomas, *Proc. Roy. Soc. (Lond.)* A300, 108 (1967).
11. L. R. G. Treloar, "The Physics of Rubber Elasticity," 2nd. ed., Oxford University Press, London, 1968, p. 156.
12. D. Barnard, L. Bateman, J. I. Cunneen and J. F. Smith, "The Chemistry and Physics of Rubberlike Substances," ed. by L. Bateman, John Wiley and Sons, New York, 1963, Chap. 17.

13. A. N. Gent and R. P. Petrich, Proc. Roy. Soc. (Lond.)
A310, 433 (1969).
14. A. N. Gent and A. J. Kinloch, J. Polymer Sci., Pt.
A-2 9, 659 (1971).
15. A. N. Gent and G. R. Hamed, J. Appl. Polymer Sci.
21, 2817 (1977).
16. A. N. Gent and G. R. Hamed, Plastics and Rubber:
Materials and Application, 3, 17 (1978); reprinted
in Rubber Chem. Technol. 51, 354 (1978).

Figure Legends

1. (Symmetrical Test Method.)
2. Test method for adhesion of an elastomer layer to glass.
3. Bonding polybutadiene (PB) to glass treated with a mixture of vinylsilane (R) and ethylsilane (R'). The elastomer layer is crosslinked and interlinked in situ by a free-radical-producing agent, dicumyl peroxide (DCP).
4. Threshold work of detachment \underline{W}_O for polybutadiene vs the fraction of vinylsilane in the mixture of vinyl and ethyl silanes used to treat a glass surface. Taken from reference 5.
5. Work of detachment \underline{W}_a vs the rate \underline{R} of peeling for partially-interlinked sheets of polybutadiene (PB), dry (●) and swollen with paraffin oil (○). Taken from reference 8.
6. Threshold work of detachment \underline{W}_O vs the degree of interlinking $\underline{\Delta v}$ between two sheets of polybutadiene. Taken from reference 8.
7. Interlinking between two sheets of polybutadiene as a result of prior exposure to air.
8. Work of detachment \underline{W}_a vs the time of exposure to air or nitrogen before the two sheets of polybutadiene were pressed together. Taken from reference 9.

Symmetrical test method

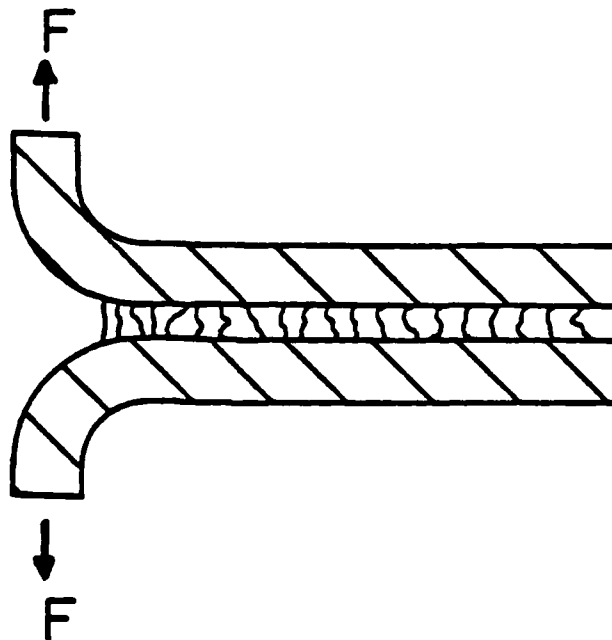
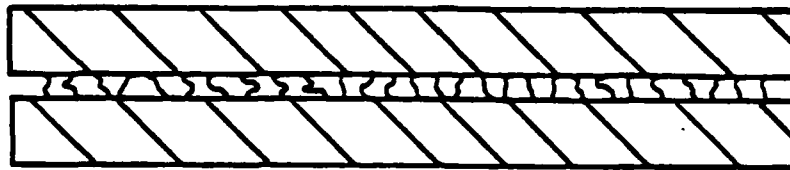
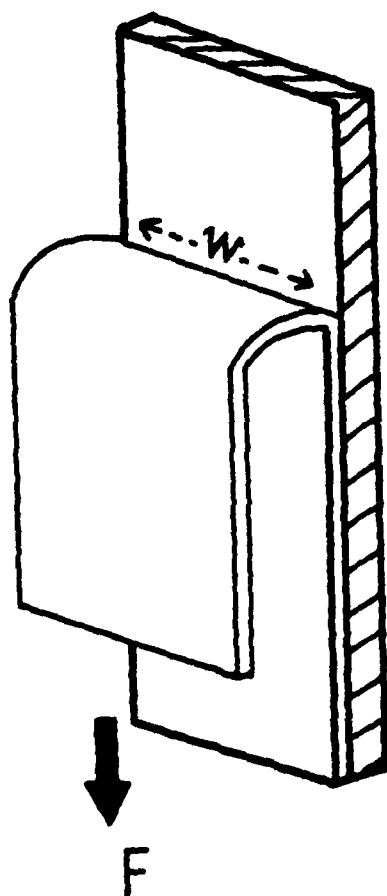


FIGURE 1



$$W_a = 2F / w$$

FIGURE 2

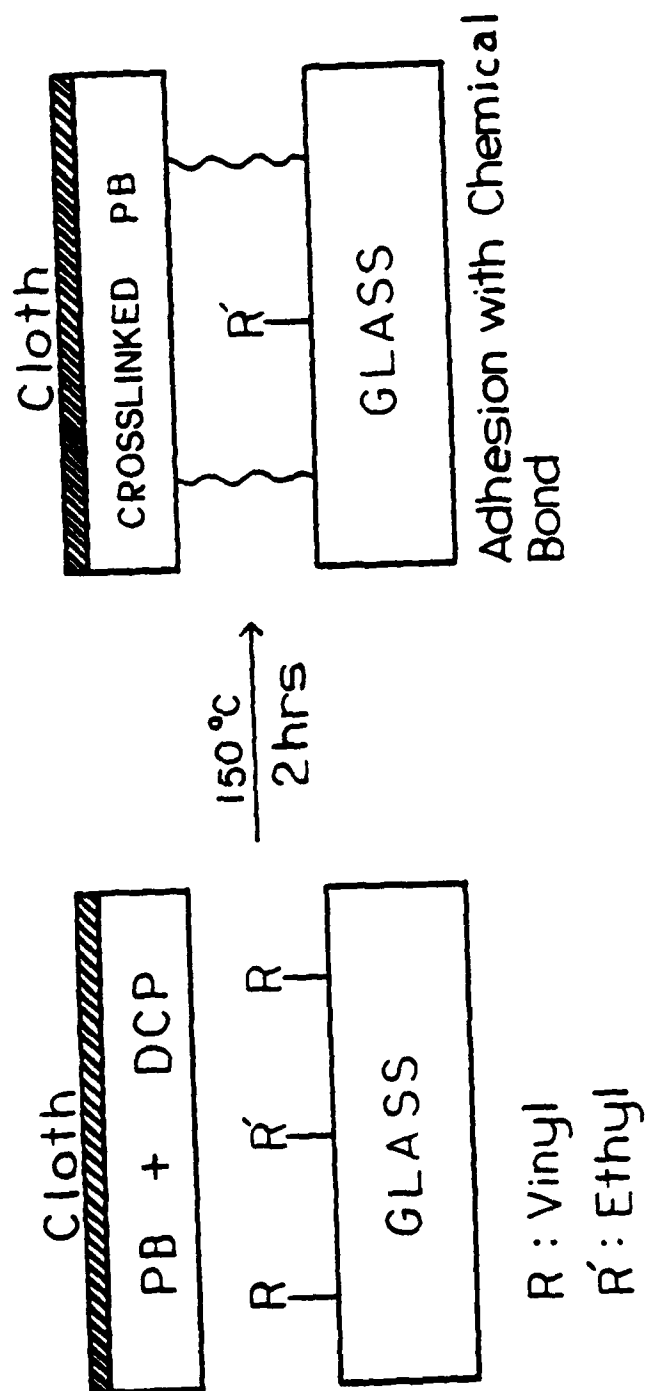


FIGURE 3

Threshold adhesion W_0
vs. vinyl silane fraction on glass

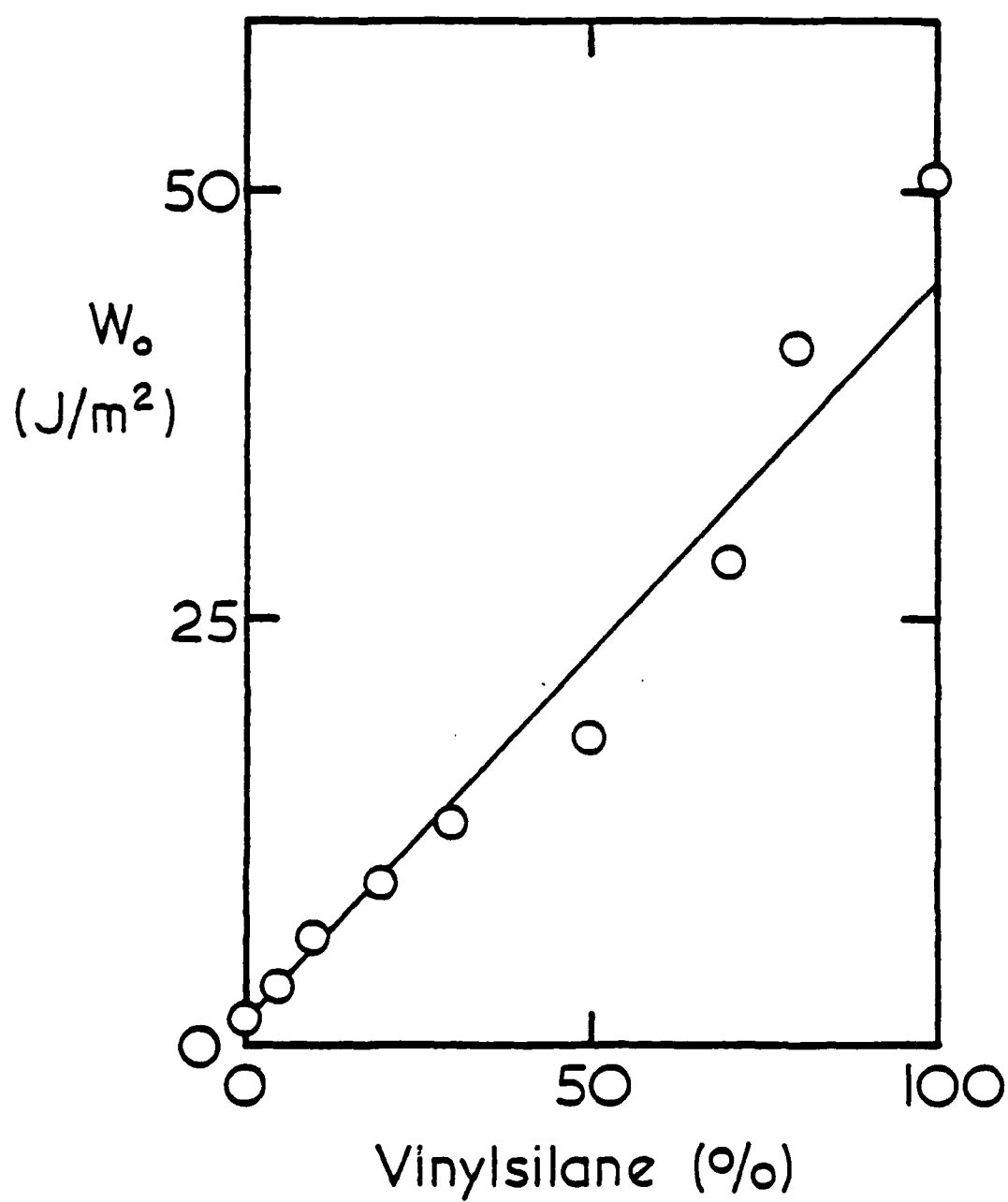


FIGURE 4

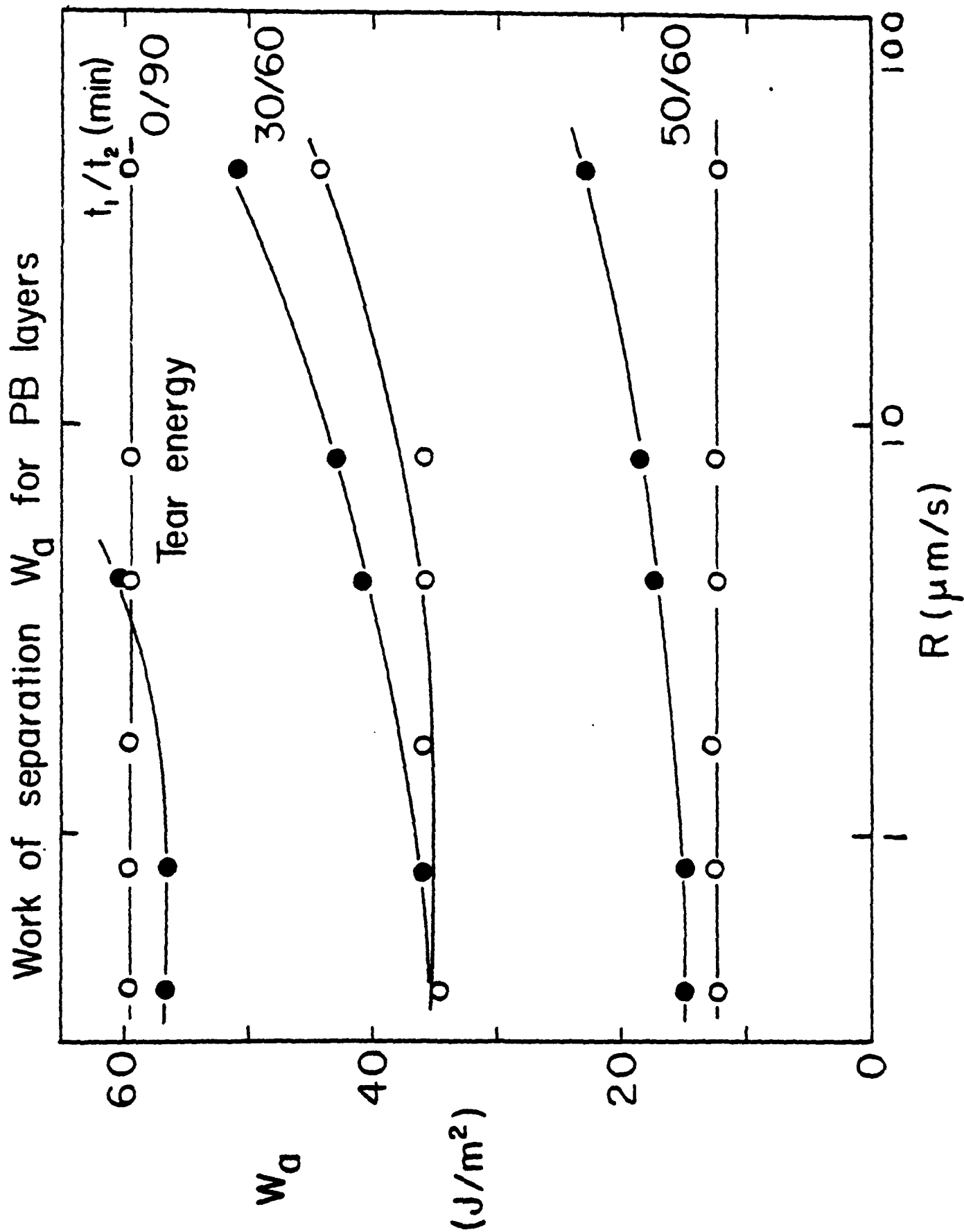
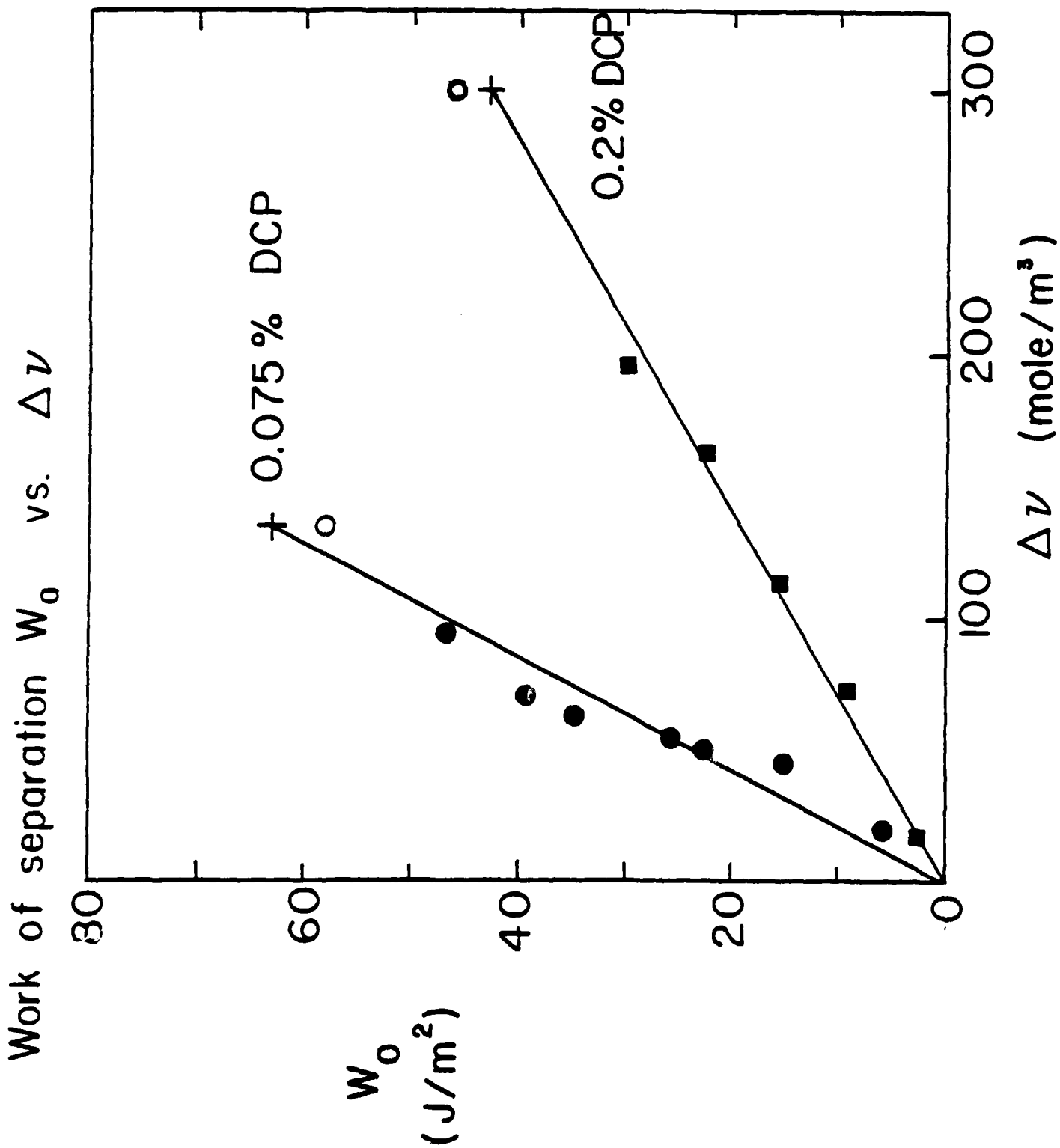


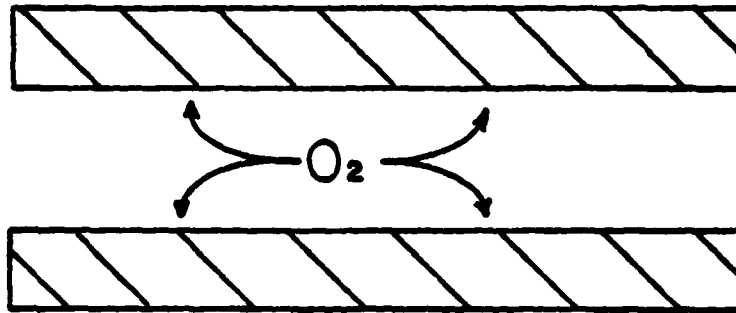
FIGURE 5



Oxidative crosslinking of polybutadiene

Step 1

Exposed to air for time t (10sec—10 days)



Step 2

Pressed together for 24 hours

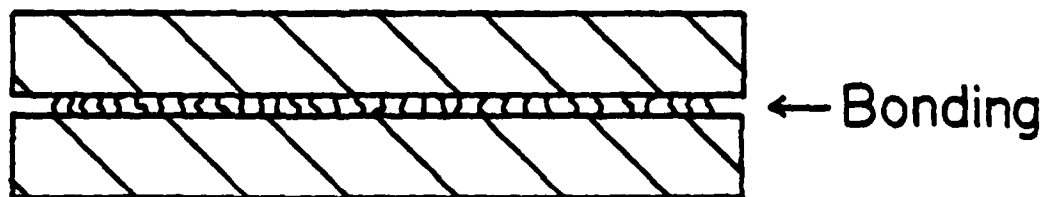


FIGURE 7

Work of separation W_a for PB layers

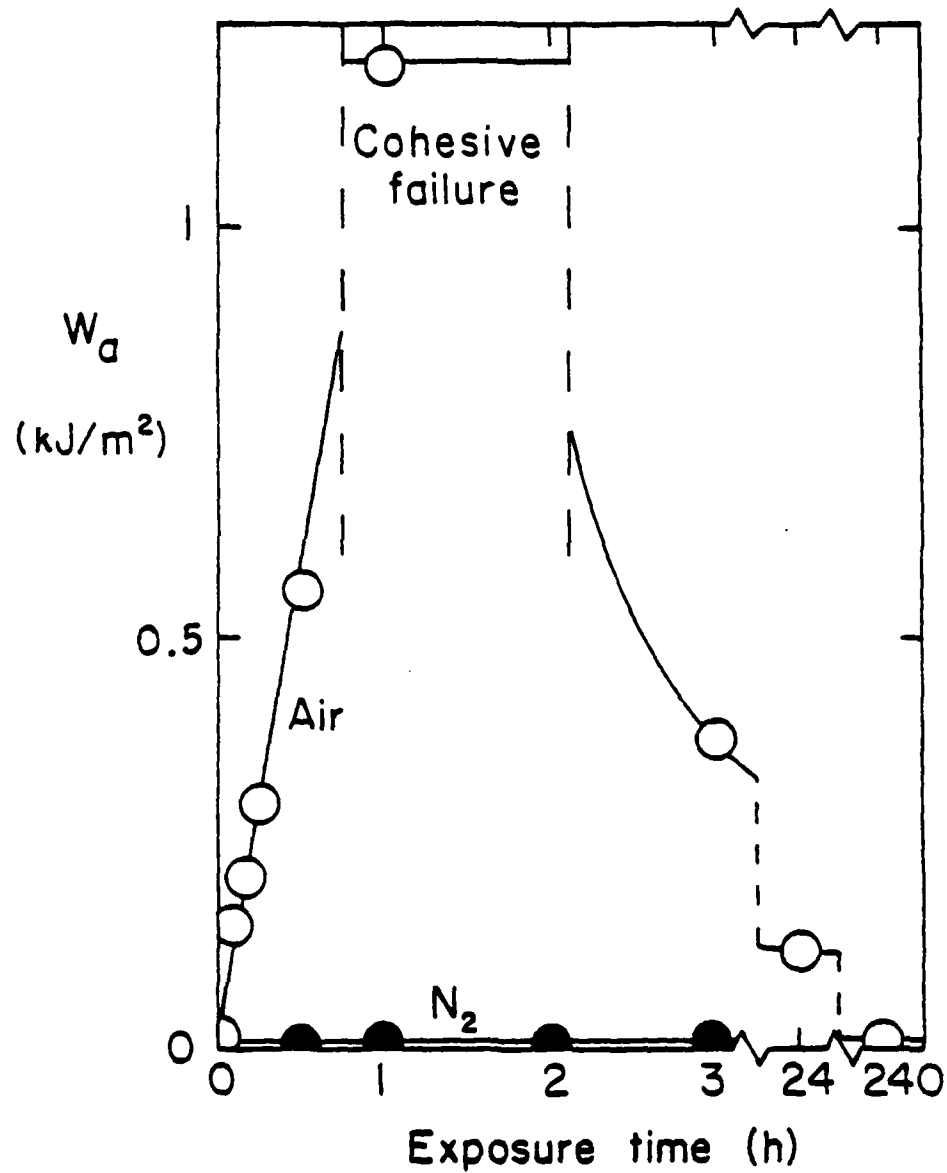


FIGURE 8

DEF:

ENERGETIC MATERIALS RESEARCHDISTRIBUTION LIST

	<u>No. Copies</u>		<u>No. Copies</u>
Assistant Secretary of the Navy (R, E, and S) Attn: Dr. R.E. Reichenbach Room 5E787 Pentagon Washington, DC 20350	1	AFATL Eglin AFB, FL 32542 Attn: Dr. Otto K. Heiney	1
Office of Naval Research Code 473 Arlington, VA 22217 Attn: Dr. R. Miller	10	AFRPL Code PACC Edwards AFB, CA 93523 Attn: Mr. W. C. Andrepont	1
Office of Naval Research Code 2008 Arlington, VA 22217 Attn: Dr. J. Enig	1	AFRPL Code CA Edwards AFB, CA 93523 Attn: Dr. R. R. Weiss	1
Office of Naval Research Code 260 Arlington, VA 22217 Attn: Mr. D. Siegel	1	Code AFRPL MKPA Edwards AFB, CA 93523 Attn: Mr. R. Geisler	1
Office of Naval Research Western Office 1030 East Green Street Pasadena, CA 91106 Attn: Dr. T. Hall	1	Code AFRPL MKPA Edwards AFB, CA 93523 Attn: Dr. F. Roberto	1
Office of Naval Research Eastern Central Regional Office 495 Summer Street Boston, MA 02210 Attn: Dr. L. Peebles Dr. A. Wood	2	AFSC Andrews AFB, Code DLFP Washington, DC 20334 Attn: Mr. Richard Smith	1
Office of Naval Research San Francisco Area Office One Hallidie Plaza Suite 601 San Francisco, CA 94102 Attn: Dr. P. A. Miller	1	Air Force Office of Scientific Research Directorate of Chemical & Atmospheric Sciences Bolling Air Force Base Washington, DC 20332	1
Defense Technical Information Center DTIC-DDA-2 Cameron Station Alexandria, VA 22314	12	Air Force Office of Scientific Research Directorate of Aero- space Sciences Bolling Air Force Base Washington, DC 20332 Attn: Dr. L. H. Caveny	1
		Anal-Syn Lab Inc. P.O. Box 547 Paoli, PA 19301 Attn: Dr. V. J. Keenan	1

DEF.

	<u>No. Copies</u>		<u>No. Copies</u>
Army Ballistic Research Labs Code DRDAR-BLP Aberdeen Proving Ground, MD 21005 Attn: Mr. L. A. Watermeier	1	Hercules Inc. Eglin AFATL/DL DL Eglin AFB, FL 32542 Attn: Dr. Ronald L. Simmons	1
Army Ballistic Research Labs ARRADCOM Code DRDAR-BLP Aberdeen Proving Ground, MD 21005 Attn: Dr. Ingo W. May	1	Hercules Inc. Magna Bacchus Works P.O. Box 98 Magna, UT 84044 Attn: Mr. E. H. DeButts	1
Army Ballistic Research Labs ARRADCOM Code DRDAR-BLT Aberdeen Proving Ground, MD 21005 Attn: Dr. Philip Howe	1	Hercules Inc. Magna Bacchus Works P.O. Box 98 Magna, UT 84044 Attn: Dr. James H. Thacher	1
Army Missile Command Code DRSME-RK Redstone Arsenal, AL 35809 Attn: Dr. R. G. Rhoades Dr. W. W. Wharton	2	HQ US Army Material Development Readiness Command Code DRCDE-DW 5011 Eisenhower Avenue Room 8N42 Alexandria, VA 22333 Attn: Mr. S. R. Matos	1
Atlantic Research Corp. 5390 Cherokee Avenue Alexandria, VA 22314 Attn: Dr. C. B. Henderson	1	Johns Hopkins University APL Chemical Propulsion Information Agency Johns Hopkins Road Laurel, MD 20810 Attn: Mr Theodore M. Gilliland	1
Ballistic Missile Defense Advanced Technology Center P.O. Box 1500 Huntsville, AL 35807 Attn: Dr. David C. Sayles	1	Lawrence Livermore Laboratory University of California Livermore, CA 94550 Attn: Dr. M. Finger	1
Ballistic Research Laboratory USA ARRADCOM DRDAR-BLP Aberdeen Proving Ground, MD 21005 Attn: Dr. A. W. Barrows	1	Lawrence Livermore Laboratory University of California Livermore, CA 94550 Attn: Dr. R. McGuire	1
Hercules Inc. Cumberland Aerospace Division Allegany Ballistics Lab P.O. Box 210 Cumberland, MD 21502 Attn: Dr. Rocco Musso	2	Lockheed Missiles and Space Co. P.O. Box 504 Sunnyvale, CA 94088 Attn: Dr. Jack Linsk Org. 83-10 Bldg. 154	1

DEF.

	<u>No. Copies</u>		<u>No. Copies</u>
Lockheed Missile & Space Co. 3251 Hanover Street Palo Alto, CA 94304 Attn: Dr. H. P. Marshall Dept. 52-35	1	Naval Research Lab Code 6100 Washington, DC 20375	1
Los Alamos Scientific Lab P.O. Box 1663 Los Alamos, NM 87545 Attn: Dr. R. Rogers, WX-2	1	Naval Sea Systems Command Washington, DC 20362 Attn: Mr. G. Edwards, Code 62R3 Mr. J. Murrin, Code 62R2 Mr. W. Blaine, Code 62R	1
Los Alamos Scientific Lab P.O. Box 1663 Los Alamos, NM 87545 Attn: Dr. B. Craig, M Division	1	Naval Sea Systems Command Washington, DC 20362 Attn: Mr. R. Beauregard SEA 64E	1
Naval Air Systems Command Code 330 Washington, DC 20360 Attn: Mr. R. Heitkotter Mr. R. Brown	1	Naval Surface Weapons Center Code R11 White Oak, Silver Spring, MD 20910 Attn: Dr. H. G. Adolph	1
Naval Air Systems Command Code 310 Washington, DC 20360 Attn: Dr. H. Mueller Dr. H. Rosenwasser	1	Naval Surface Weapons Center Code R13 White Oak, Silver Spring, MD 20910 Attn: Dr. R. Bernecker	1
Naval Explosive Ordnance Disposal Facility Indian Head, MD 20640 Attn: Lionel Dickinson Code D	1	Naval Surface Weapons Center Code R10 White Oak, Silver Spring, MD 20910 Attn: Dr. S. J. Jacobs	1
Naval Ordnance Station Code 5034 Indian Head, MD 20640 Attn: Mr. S. Mitchell	1	Naval Surface Weapons Center Code R11 White Oak, Silver Spring, MD 20910 Attn: Dr. M. J. Kamlet	1
Naval Ordnance Station Code PM4 Indian Head, MD 20640 Attn: Mr. C. L. Adams	1	Naval Surface Weapons Center Code R04 White Oak, Silver Spring, MD 20910 Attn: Dr. D. J. Pastine	1
Dean of Research Naval Postgraduate School Monterey, CA 93940 Attn: Dr. William Tolles	1	Naval Surface Weapons Center Code R13 White Oak, Silver Spring, MD 20910 Attn: Dr. E. Zimet	1
Naval Research Lab Code 6510 Washington, DC 20375 Attn: Dr. J. Schnur	1		

DEF.

6/80

4

	<u>No. Copies</u>		<u>No. Copies</u>
Naval Surface Weapons Center Code R101 Indian Head, MD 20640 Attn: Mr. G. L. MacKenzie	1	Naval Weapons Center Code 388 China Lake, CA 93555 Attn: D. R. Derr	1
Naval Surface Weapons Center Code R17 Indian Head, MD 20640 Attn: Dr. H. Haiss	1	Naval Weapons Center Code 388 China Lake, CA 93555 Attn: Dr. R. Reed Jr.	1
Naval Surface Weapons Center Code R11 White Oak, Silver Spring, MD 20910 Attn: Dr. K. F. Mueller	1	Naval Weapons Center Code 385 China Lake, CA 93555 Attn: Dr. A. Nielsen	1
Naval Surface Weapons Center Code R16 Indian Head, MD 20640 Attn: Dr. T. D. Austin	1	Naval Weapons Center Code 3858 China Lake, CA 93555 Attn: Mr. E. Martin	1
Naval Surface Weapons Center Code R122 White Oak, Silver Spring, MD 20910 Attn: Mr. L. Roslund	1	Naval Weapons Center China Lake, CA 93555 Attn: Mr. R. McCarten	1
Naval Surface Weapons Center Code R121 White Oak, Silver Spring, MD 20910 Attn: Mr. M. Stosz	1	Naval Weapons Support Center Code 5042 Crane, Indiana 47522 Attn: Dr. B. Douda	1
Naval Weapons Center Code 3853 China Lake, CA 93555 Attn: Dr. R. Atkins	1	Rohm and Haas Company 723-A Arcadia Circle Huntsville, Alabama 35801 Attn: Dr. H. Shuey	1
Naval Weapons Center Code 3205 China Lake, CA 93555 Attn: Dr. L. Smith	1	Strategic Systems Project Office Dept. of the Navy Room 901 Washington, DC 20376 Attn: Dr. J. F. Kincaid	1
Naval Weapons Center Code 3205 China Lake, CA 93555 Attn: Dr. C. Thelen	1	Strategic Systems Project Office Dept. of the Navy Room 1048 Washington, DC 20376 Attn: Mr. E. L. Throckmorton Mr. R. Kinert	2
Naval Weapons Center Code 385 China Lake, CA 93555 Attn: Dr. A. Amster	1	Thiokol Chemical Corp. Brigham City Wasatch Division Brigham City, UT 84302 Attn: Dr. G. Thompson	1

	<u>No. Copies</u>		<u>No. Copies</u>
USA ARRADCOM DRDAR-LCE Dover, NJ 07801 Attn: Dr. R. F. Walker	1	Georgia Institute of Technology Office of Research Administration Atlanta, Georgia 30332 Attn: Professor Edward Price	1
USA ARRADCOM DRDAR-LCE Dover, NJ 07801 Attn: Dr. N. Slagg	1	Univ. of Utah Dept. of Mech. & Industrial Engineering MEB 3008 Salt Lake City, Utah 84112 Attn: Dr. Stephen Swanson	1
U.S. Army Research Office Chemistry Division P.O. Box 12211 Research Triangle Park, NC 27709	1	Space Sciences, Inc. 135 Maple Avenue Monrovia, CA 91016 Attn: Dr. M. Farber	1
Institute of Polymer Science University of Akron Akron, OH 44325 Attn: Professor Alan N. Gent	1	Washington State University Dept. of Physics Pullman, WA 99163 Attn: Professor G.D. Duval	1
SRI International 333 Ravenswood Avenue Menlo Park, CA 94025 Attn: Dr. Y.M. Gupta	1	Univ. of Maryland Department of Mechanical Eng. College Park, MD 20742 Attn: Professor R.W. Armstrong	1
Graduate Aeronautical Lab. California Institute of Technology Pasadena, CA 91125 Attn: Professor W.G. Knauss	1	The Catholic University of America Physics Department 520 Michigan Ave., N.E. Washington, D.C. 20017 Attn: Professor T. Litovitz	1
Pennsylvania State University Dept. of Mechanical Engineering University Park, PA 16802 Attn: Professor Kenneth Kuo	1	Sandia Laboratories Division 2513 P.O. Box 5800 Albuquerque, N.M. 87185 Attn: Dr. S. Sheffield	1
Office of Naval Research 800 N. Quincy St. Arlington, VA 22217 Attn: Dr. G. Neece Code 472	1	IBM Research Lab. K42.282 San Jose, CA 95193 Attn: Dr. Thor L. Smith	1
Thiokol Corp. Huntsville Huntsville Div. Huntsville, AL 35807 Attn: Mr. J.D. Byrd	1	California Institute of Tech. Dept. of Chemical Engineering Pasadena, CA 91125 Attn: Professor N.W. Tschoegl	1
Washington State University Dept. of Physics Pullman, WA 99163 Attn: Prof. T. Dickinson	1	Northwestern University Dept. of Civil Engineering Evanston, IL 60201 Attn: Professor J.D. Achenbach	1
University of California Dept. of Chemistry 405 Hilgard Avenue Los Angeles, CA 90024 Attn: Prof. M.F. Nicol	1	Office of Naval Research Structural Mechanics Program Arlington, VA 22217 Attn: Dr. N.L. Basdekas, Code 474	1

DEF.

No. Copies

University of California 1
Berkeley, CA 94720
Attn: Prof. A.G. Evans

Texas A&M Univ. 1
Dept. of Civil Engineering
College Station, TX 77843
Attn: Professor Richard A. Schapery

SRI International 1
333 Ravenswood Ave.
Menlo Park, CA 94025
Attn: Mr. M. Hill

Los Alamos Scientific Laboratory 1
Los Alamos, NM 87545
Attn: Dr. J.M. Walsh

Rockwell International 1
12214 Lakewood Blvd.
Downey, CA 90241
Attn: H. M. Clancy, Mail Stop AB 70

ONR Resident Representative 1
Ohio State University Research Center
1314 Kinnear Road
Columbus, Ohio 43212
Attn: Joseph Haggard, Department
of the Navy

ATE
LMED
-8